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HIGH TEMPERATURE PROTECTIVE COATINGS  
DEVELOPMENTS

at

GENERAL DYNAMICS/FORT WORTH, TX.

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J. E. Burroughs

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Prepared for the Seventh

NASA-ASD Sponsored

REFRACTORY COMPOSITES WORKING GROUP MEETING

March 11-14, 1963

Palo Alto, California

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## I. Objective

The coating program being carried out at GD/FW is being done on a continuous basis. This report covers the program for the last fiscal year for presentation to this group. The various portions of the research are presented at their present stage of development. The overall object of our investigation, which has not been realized as yet is to develop and evaluate a slurry or spray-on intermetallic coating (Sylcor type) for elevated temperature oxidation protection of refractory metal alloys subjected to re-entry vehicle environments. The thermal environment considered was 5 hours at 3300<sup>0</sup>F for the tantalum alloy and 20 hours at 2300<sup>0</sup>F for the columbium alloy.

## II. Background

The pack cementation process and its application to refractory metal alloys was studied in FY1961. Variables such as time, temperature and elemental ratios from available reports were analyzed to try to optimize pack variables in processing. Three types of coatings appeared to be most promising: chromium plus

titanium, chromium plus titanium plus silicon, and chromium plus silicon. Work accomplished in FY1961 consisted of numerous pack cementation runs to establish the best techniques for lay-up, packaging, cleaning of details, etc. Coatings obtained have shown steady improvement as evidenced by appearance and microstructure. Due to the limited funds available the coated specimens were examined visually and some limited oxidation tests were conducted.

At the SAMPE-ASD sponsored "Ceramics and Composite Coatings Symposium" in Dayton November 1961, the preliminary results of Sylcors work on slurry-dip, paint, or spray-on intermetallic diffusion coatings were reported. In addition, the Martin-Marietta Company representative reported on utilizing this type of coating on their ASD contract "Refractory Metal Structure" (brazed and welded sandwich) for 3300-3400°F operation.

This intermetallic diffusion coating on tantalum has exhibited some resistance to over 3000°F for short time exposures. The Martin Company personnel also reported exposure to

3450°F for fifteen (15) minutes and with some self healing characteristics. It has been theorized that the aluminum in this coating induces self-repair by being transported from the  $TaAl_3$  layer through the liquid Sn-rich phase to the  $Al_2O_3$  barrier.

Because of the encouraging results obtained by this technique, and ease of application it was decided to investigate the Sylcor type coating in FY1962 instead of continuing the more cumbersome three component pack cementation development. The Sylcor diffusion type coating would lend itself more readily to large, complex components than the other processes.

### III. Program

#### A. Development of Intermetallic Coatings

During the last year the Al-Sn intermetallic coating for columbium and tantalum alloys was investigated at GD/FW. D-31 and FS-82 columbium and Ta-10W tantalum alloys were used in the investigation. Initial efforts were intended to produce a workable coating by establishing the processing variables, ie., vehicle, vehicle thinning, vehicle-powder

mixture, diffusion temperature and time at temperature. Once the coating had been produced and effects of variables were known, additional research was initiated to modify this coating with more refractory elements or compounds to increase its resistance to elevated temperature for longer periods of time. As the program progressed investigations into duplex diffusion coatings were also conducted to obtain greater thickness.

The coatings were diffused in a tube furnace under purified argon atmosphere.

Screening tests used in coating development were:

1. Thickness
  - (a) coating
  - (b) diffusion layer
2. Appearance
3. Microstructure
4. Bend ductility
5. Oxidation Resistance: Center of  $1/2 \times 1$  inch specimen heated by natural gas-oxygen flame in air to temperatures up to  $2500^{\circ}\text{F}$  as determined by optical pyrometer readings taken on unheated side of specimen.

B. Evaluation of GD/FW Developed Intermetallic Coating

The more promising coatings for columbium and tantalum alloys were evaluated by the following tests.

1. Oxidation resistance at elevated temperature in moving air.
  - a. Continuous exposure
  - b. Thermal shock resistance to multiple exposure.
2. Self-repairability - Scribe lines were marked on oxidation specimens and ability to self-repair was observed.
3. Tensile test at temperature.
  - a. The best coating for each alloy was evaluated by coating columbium and tantalum tensile specimens and testing at the following temperatures.  
D-31 columbium alloy RT, 1500, 2500°F  
Ta-10W alloy RT, 1000, 2000, 2800, 3300°F
  - b. General Telephone & Electronics Laboratory (Sylcor) coated tensile specimen were also evaluated at the same test temperatures.

#### IV. Summary of Results

Saturated solutions (refluxed overnight) of PVA in water, methyl alcohol, isopopyl alcohol, and acetone were found to be unsatisfactory for coating application. A commercial grade of lacquer was used for the greater portion of the program with some degree of success, but in many cases duplex treatments were necessary to obtain a coating of adequate thickness. The use of a low residue lacquer, Raffi and Swanson No. 1830, greatly simplified the application of the coatings.

Early in the program it appeared that the columbium base alloys would be more easily coated than the tantalum alloys. Portions of D-31 and Ta-10W which were dipped into molten 50Al-50 Sn at 1900°F for one hour are shown in Figure 1. The diffusion zone on the D-31 is even and clearly defined. The tantalum had a narrow diffusion zone along most of the specimen, but highly localized attack occurred adjacent to the liquid surface. In the application of slurry dipped coatings, the tantalum was more easily coated. It appears that a small amount of



TA-10W (LEFT) AND TA-11 (RIGHT) (TA-10W AND TA-11 ARE AL-CLAD FOR  
3% ROTN. AT 1800°F)

oxide enhances the diffusion in tantalum.

A composition of 50 Al-50 Sn was found to be more resistant to oxidation, but 75Sn-25Al was a more easily applied coating. Work has not been completed in this area, as yet, but it is felt that a composition between these two will produce the optimum coating for this system. The 50Al-50Sn coating on D-31 columbium alloy has withstood 2000°F for 100 hours, 2300°F for 4-8 hours, and 2500°F for 10-15 minutes. The same coating on Ta-10W withstood 2300°F for up to 50 hours and 2500°F for 3 hours. Failures usually originated from the holes used to suspend them during coating. The edges had been carefully rounded and the holes chamfered.

A typical failure, shown in Figure 2, occurred after 4 hours at 2200°F to the 50 Al-50Sn coated FS-82 columbium alloy specimen. The areas shown in the two micros are identical, only the method of lighting is different. The diffusion layer which appears bright and only slightly different in color from the substrate under bright field, appears as either



FIGURE 2 (100 X)

FIGURE 1. Micrograph of the cross-section of the material, showing the dark, textured central region and the lighter, granular outer layer.

dark or light grains under polarized light. This birefringence is due to the anisotropic nature of the intermetallic, probably  $\text{CbAl}_3$ . The areas which appear dark under bright field and speckles under polarized light are the oxidized portions of the coating. Note the blob of oxide formed on the edge of the specimen and the under cutting of the coating adjacent to the failure. The oxide build up which had started only minutes before was growing at a very rapid rate when the specimen was removed from the furnace. Note also that the coating has been oxidized to the substrate in one area of the specimen face. Failure was probably imminent at this point.

The basic tin-aluminum coating was modified with additions of copper, chromium, titanium and zirconium. The latter two elements were not absorbed into the alloy on diffusion when added as elemental powders. Subsequent additions were made in the form metal hydrides. The limited alloy modification work done to this time can only be considered to be indicative, but the most promising additions have been chromium and titanium.

The latter formed a visible oxide very quickly, but it seemed to be quite tough and resistant to further oxidation.

The tensile testing, to date, has been limited to D-31 columbium alloy to 2200°F in partial vacuum. The controls for this heat of material have not been tested as yet, but based on other heats that have been tested there is no extremely deleterious effect. The greatest effect is to the yield strength which is somewhat lowered. The ultimate strength is reduced only slightly and ductility remains excellent.

#### V. Current Efforts

During the coming year work will be continued on the aluminum tin system and its modifications. The new low residue lacquer seems to impart a greater fluidity to the coating on diffusion which will necessitate a further investigation of these variables. Although the aluminum-tin coating provides excellent protection to 2000°F, above this temperature it seems to be deteriorating rapidly. The possibility of utilizing another

eutectic to provide for better self healing characteristics will be investigated. Copper forms a higher melting eutectic with aluminum and in addition forms solid solutions with some of the other elements. Silicon has been used by several investigators with some success. Attempts to improve the oxidation resistance of the coatings with chromium, titanium, and zirconium will be continued and hafnium will be included. The effect of the coatings on the mechanical properties of the substrate will be further investigated. Tests will be made on the effect of low temperature on coatings containing tin. Tin undergoes a transformation to its enantiotropic form, a tin powder, which might preclude its use in cold environments.

Planning is complete and hardware is available for a creep oxidation resistance test set-up. The coated specimen will be resistance heated in moving air while loaded to a stress that will cause creep. Programming will be included for the three variables, temperature, loading and atmosphere, to permit cycling in addition to steady state effects. This should be an

excellent test of the coatings ability to  
withstand service conditions.